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DESORPTION OF BARIUM OXIDE MOLECULES FROM TUNGSTEN IN A STRONG ELECTRIC FIELD

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The field desorption of BaO molecules from tungsten was studied over a temperature range of 80 - 1200° K by means of Müller's field emission microscope. Müller's experiments for Ba on W were also repeated over the same temperature range for comparison. The dependence of the square root of the field strength upon the temperature at low coverages is presented in Fig.4. The theory of ion vaporization over the Schottky barrier, when applied to the case of BaO and Ba on W, predicts the following: 1) The field desorption of BaO must occur as BaO^{+} within the 80 - 400° K range and as BaO^{++} within the 500 - 1100° K range. 2) Barium must be field-desorbed from W in the form of singly-charged ions over the 80 - 300° K and 1000 - 1200° K regions, and as doubly-charged ions at 300 - 1000° K.

Author

1. Introduction

The BaO-W system with its good emissive properties is of major importance to cathode electronics and hence has been the object of numerous studies. It may also be of interest to investigate the desorption of BaO molecules from W under the action of a strong electric field (self-desorption), since a series of studies has shown the great value of this method in the clarification of prob-

* Numbers in the margin indicate pagination in the original foreign text.

lems of the interaction between adsorbed particles and the adsorbent as well as between the particles themselves (Bibl.1, 2).

It may also be expected that studies of the BaO-W system will contribute to the refinement and expansion of the current knowledge of self-desorption, since the self-desorption of polar molecules, which include BaO (Bibl.3), has never been thoroughly investigated. Previous studies of compounds of the KCl type on W have only established that the field desorbs the K and Cl ions separately (Bibl.4).

For these reasons, we found it of interest to investigate the self-desorption of BaO from W.

2. Experimental Procedure

The self-desorption of molecules of BaO from W was investigated with the aid of the Müller point field emission microscope. The final evacuation of the tubes was accomplished by sputtering getters (molybdenum, titanium, or tantalum); the cylinders containing the getters could be immersed in liquid nitrogen. The barium getter was also sputtered. Field-emission images and the edge flow from the tungsten point did not change markedly over tens of hours, the total pressure of the residual gases, measured by a Bayard-Alpert gage, being approximately 3×10^{-9} mm Hg. We placed BaO and Ba sources in the tubes. The purity of these sources was previously checked with a mass spectrometer by B.O.Chuykov. The vaporizers were thoroughly degassed. Sputtered BaO and Ba were poured sideways on a tungsten point at room temperature. After this, the point was heated to 1000 - 1100°K so that its entire upper surface was covered by a film of BaO or Ba.

The concentration h of particles on the surface of the point was estimated

on the basis of the known relations $\Delta\varphi = \Delta\varphi(n)$ (Bibl.5), where $\Delta\varphi$ is the variation in the work function of the adsorbent. The work function was calculated according to the slope of the Fauler-Nordheim lines.

As is known (Bibl.1), the conditions for self-desorption of electropositive particles are more favorable the lower the degree of deposition Θ. Therefore, the stripping of the adsorbed film increases abruptly in the presence of a /66 gradual increase in the electric field, which gives reason to believe that (for a fixed observation time) the desorbing field for a given T and Θ for a given face $\{hkl\}$: $F_{d\{hkl\}} = f(\Theta, T)$. In these investigations the desorbing field was the principal quantity measured.

We measured the desorbing field by alternately switching the field-emission microscope to the self-desorption ("plus" on the tungsten point) and field-emission regimes (Bibl.1, 6). The self-desorption stress gradually increased until the field-emission image revealed stripping of the film. Although this method is less productive than the impulse method (Bibl.7), it is much more advantageous in the high-temperature region, where the migration of adatoms over the point and the thermoelectron emission are considerable.

To determine the radius of the tungsten point and the strength of the electric field near the surface of the point, the Drexler and Henkel approximation (Bibl.8) was used. The error in determining the field by this method is estimated at 10 - 15% (Bibl.6, 8), whereas the relative error in measurements of the desorption stress in our investigations was of the order of several percent. It should also be emphasized that the atomic structure of the surface was not taken into account in calculating the field.

3. Experimental Results

Figure 1 shows the field-emission images of the pure single crystal of W

(Fig.1a), a BaO layer on W (Fig.1b, $\Delta\varphi$ = 0.3 ev), a Ba layer on W (Fig.1c, $\Delta\varphi$ = = 0.4 ev), and a layer of oxygen on W [Fig.1d, photograph taken from (Bibl.9)]. Noteworthy is the variation, in the field-emission images, of BaO and Ba films on W in the presence of approximately identical $\Delta\varphi$ (Fig.1b and c); in the first case, large dark areas surround the faces {001} and {111}, while in the second case the faces {111} are light. There are, however, certain common features in the images of the adsorption of BaO and O layers on W (Fig.1b and d): the dark areas in Fig.1b {001} and {111} are light in Fig.1d, whereas the areas along the zones {111} which are brightest in Fig.1b are darkest in Fig.1d. Hence, in a way, the micrograph 1d is a negative of the micrograph 1b. This analysis suggests that the selectivity of adsorption of BaO on W may be primarily determined by the binding energy between the oxygen portion of the molecule and a given surface of W (at any rate, in the presence of low degrees of deposition).

It is of fundamental significance in this investigation to find an answer to the question whether self-desorption is accompanied by a degradation of the BaO molecule [as in the case of KCl on W (Bibl.4)] or whether it is stripped off in its entirety. Figure 2 presents two microphotographs of a point, obtained after self-desorption of a BaO film at T = 300° K (Fig.2a) and after thermal desorption of such a layer by heating it for 5 sec at 1800° K (Fig.2b; in both cases, the initial $\Delta\varphi \approx 1$ ev). The desorption field was approximately 200 mv/cm (mean of the desorption fields for barium and oxygen).

After self-desorption, the field-emission image (Fig.2a) corresponds to nearly pure W; the changes in the shape of the face (011) are minor, a fact still difficult to explain. It may be that the point does not remain quite pure or that its surface becomes etched to some extent. At the same time, Fig.2b clearly shows traces of the contamination of the point by oxygen (Bibl.9). At

1800° K, according to Ptushinskiy and Chuykov (Bibl.10), the probability of a thermal dissociation of BaO on W is several percent. Figure 2b indicates that

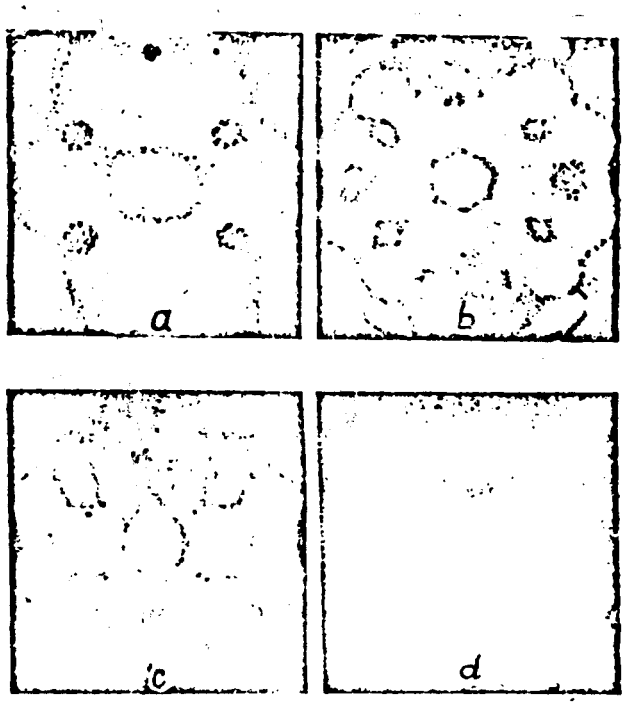

Fig.1
a - Field-emission image of pure W single crystal;
b - BaO on W ($\Delta\varphi \sim 0.3$ ev); c - Ba on W ($\Delta\varphi \sim 0.4$ ev);
d - Oxygen-coated tungsten point (Bibl.9)

the dissociation of even such a small portion of the BaO molecules that succeeded in "surviving" on the tungsten surface at ~1800° K already leads to characteristic changes in the image [compare also the case of SrO on W (Bibl.11)]. /67 These facts indicate that the probability of a dissociation of BaO during its self-desorption from W is in any case $\lesssim 10^{-2}$, with the greater portion of the BaO molecules failing to dissociate while they are stripped off by the field. In this manner, the BaO-W system differs from the KCl-W system (Bibl.4). Note that the probability of thermal dissociation of compounds of the KCl type is great even at comparatively low temperatures, a fact often utilized in studies

of surface ionization. Molecules of BaO, on the other hand, are desorbed as entities to as high a temperature as T ≈ 1700° K (Bibl.10). Hence, there exists

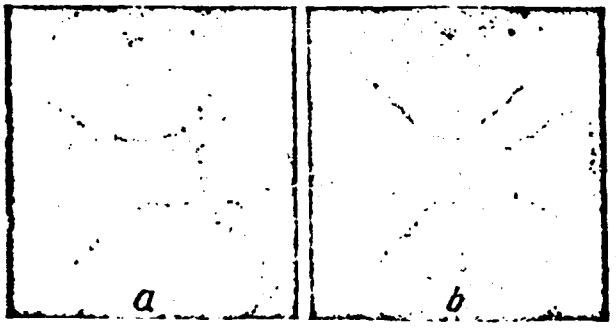

Fig.2
a - Image of point after self-desorption of BaO layer at T = 300° K by a field of ~200 mv/cm; b - Image of point after thermal desorption of BaO (1800° K, 5 sec). In both cases, initial $\Delta\varphi \approx 1$ ev.

a definite analogy between the dissociation of molecules during self-desorption and thermal desorption.

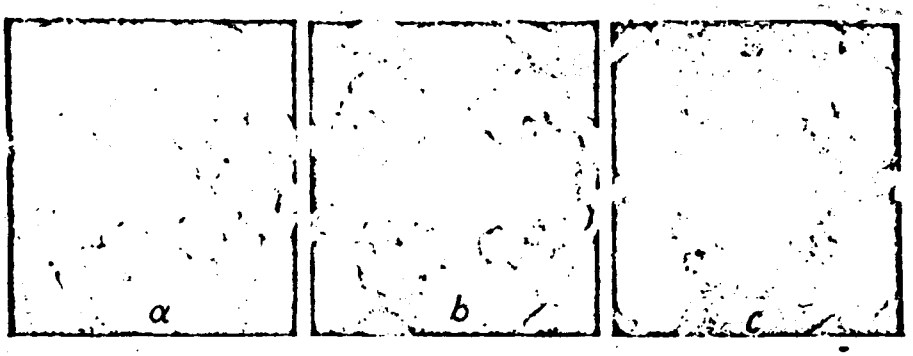

Fig.3 Self-Desorption of BaO from W
a - $F_d \approx 100$ mv/cm; b - $F_d \approx 110$ mv/cm; c - $F_d \approx 125$ mv/cm

Figure 3 illustrates the development of self-desorption of BaO from a /68 tungsten point during a gradual increase in stress (T = 300° K, $\Delta\varphi \approx 02$ ev). A field of the order of 90 mv/cm does not change the image. A field of approxi-

mately 100 mv/cm strips off the BaO film in the neighborhood of the (011) face (Fig.3a). At fields of the order of 110 - 115 mv/cm, the dark areas expand in the direction of the {111} zones (Fig.3b). In the presence of fields of approximately 120 mv/cm, the BaO film is maintained only around the {121} zones (Fig.3c). The self-desorption of the BaO adsorbed film ("adfilm") on the entire upper surface of the point decays in the presence of fields of ~130 mv/cm (taking into account the field decrease at a distance from the axis of the point).

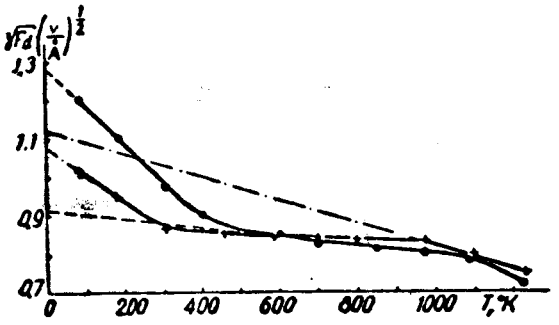

Fig.4 Desorbing Field in the Neighborhood of the Face (011), as a Function of the Temperature, at $\Theta \approx 0.1$, t = 5 sec
o - BaO on W; × - Ba on W

Figure 4 shows the desorption field for BaO on W in the vicinity of the face (011), as a function of the temperature at $\Delta\varphi \approx 0.2 - 0.3$ ev. In all cases, the desorption time was 5 sec.

With the object of comparing the BaO-W system with the Ba-W system, we also partly reproduced Müller's experiments with Ba on W (Bibl.6, 12), measuring the dependence of $\sqrt{F_d} + f(T)$ over the range of 80 - 1200° K. These data are marked by crosses in Fig.4. In the temperature range of 300 - 1200° K, to which Müller's investigations pertained, our findings are in good agreement with his data (Bibl.6, 12).

It is noteworthy that, at $T \geq 500^{\circ}$ K, the curves for BaO and Ba are much more closely spaced. However, the pattern of self-desorption in these two cases differs markedly.

Studies of the relation of the desorbing field with the degree of deposition Θ for BaO on W showed that the increase in F_d with increasing Θ is much slower in this case than in the case of Ba on W. Thus, at $T = 300^{\circ}$ K, the /69 BaO film which reduces the work function of tungsten to 2.3 ev [a value close to saturation (Bibl.5)] is stripped off in the neighborhood of the (011) zone

Fig.5
a - Image of mixed layer (BaO + Ba) on W; b - $F_d \approx 82$ mv/cm, desorption of Ba atoms from mixed layer, $T = 300^{\circ}$ K;
c - Pattern of self-desorption of pure Ba, $F_d \approx 78$ mv/cm

by a field approximately 18 mv/cm stronger than in the presence of low degrees of deposition ($\Delta\varphi \approx 0.2$ ev, $F_d = 96$ mv/cm). Thus, the field increase for BaO is approximately 20%, whereas, according to another paper (Bibl.6), it reaches 80 - 100% for barium on tungsten.

We also observed self-desorption from tungsten for mixed layers (BaO + Ba). BaO was sputtered from one side on the tungsten point, and barium from the other side. The doses of these substances were such that each of them reduced the work function by 0.3 - 0.4 ev. The field-emission pattern obtained after heat-

ing the point is shown in Fig.5a. The further procedure was conventional. It was found that, at T = 300° K and in the presence of roughly the same fields as those at which pure Ba films are desorbed from W, barium is desorbed from the mixed layers (Fig.5b). This causes the appearance of dark spots on the image in the same areas in which they are observed during the desorption of pure Ba (Fig.5c). Subsequently, after the field is increased by 15 - 20%, the BaO film also is stripped off (cf. Fig.3). Hence, adsorbed particles of BaO and Ba on W, in first approximation, behave independently with respect to self-desorption. A similar independence of the influence of BaO and Ba in their mixed layers on the work function of W was established elsewhere (Bibl.13).

4. Discussion of Results

Müller and Gomer (Bibl.1, 2, 14) treated the self-desorption of electropositive elements (Ba and Th) from W as the vaporization of the ions present on the metal surface, across the potential barrier reduced by the Schottky effect.

Considering the similarity between the self-desorption (Fig.4) and adsorption (Bibl.5) characteristics of BaO and Ba on W, and also considering that a BaO molecule is adsorbed and desorbed as a whole (Bibl.15), we will attempt to apply this theory to the case described here. It must be emphasized, however, that both the applicability of this theory to the BaO-W system and its conclusions still require thorough verification.

The expression for the desorbing field in the case of electropositive atoms (Bibl.1, 2, 14) is as follows:

$$\sqrt{F_d} = \frac{Q_{10} + nFx_0}{3.8n^{1/3}} - T\frac{\log_{10}(t\nu)}{19000n^{1/3}}, \qquad (1)$$

where F_d is the field, in v/Å; Q_{10} is the heat of evaporation of an ion in a /70

zero field (in ev); n is the multiplicity of ion charge; T is the temperature in degrees Kelvin; t is the desorption time; ν is the frequency factor; x_0 is the distance between the equilibrium state of the ion and the surface (in Å).

Since the term nFx_0 is small, the function $\sqrt{F_d} = f(T)$ must run a straight-line course with a slope of $-\log_{10} t\nu/19000\, n^{3/2}$ and with $\frac{Q_{i0}}{3.8n^{3/2}}$ as the point of intersection of the ordinate. As can be seen from Fig.4, the curves for BaO and Ba on W actually form a series of rectilinear segments (two for BaO and three for Ba).

On the basis of the determination of Q_{i0} and ν, Gomer (Bibl.14) made the assumption that the medium-temperature segment of the curve of $\sqrt{F_d} = f(T)$ for Ba corresponds to the desorption of doubly charged ions, and the high-temperature segment, to the desorption of singly charged ions. Since the prolongation of the investigated portion of the curve for Ba ($T = 80 - 300^\circ K$) intersects the ordinate at roughly the same point as the prolongation of the high-temperature portion (Fig.4), the theory leads to the conclusion that, at low as well as at high temperatures, Ba is desorbed in the form of singly charged ions. From the slope of the low-temperature segment of the curve for Ba, we obtain $\nu \approx 4 \times 10^{12}$ sec^{-1}. The curve for BaO, as noted previously, greatly resembles the curve for Ba. Assuming $n = 1$, we obtain $Q_{i0} \approx 5.0$ ev, $\nu \approx 10^{13}$ sec^{-1} for the low-temperature segment of the curve of BaO on W. Let us recall that, in accordance with the theory of absolute reaction velocities (Bibl.16), we have $\nu = \varkappa e\, e^{\frac{\Delta S}{k}}, \frac{kT}{h}$, where $\varkappa$ is the transmission coefficient, ΔS is the activation entropy for transition to the active-complex state. Therefore, ν may strongly differ from $\frac{kT}{h} \sim 10^{12} - 10^{13}$ sec^{-1}.

For singly charged ions, $Q_{i0} = Q_a + V_i - \varphi$, where Q_a is the heat of evaporation of neutral atoms, V_i is the ionization potential. Taking $Q_a = 5.1$ ev

(Bibl.5), $\varphi_{011} \approx 5.0$ ev, we will obtain from $Q_{10} \approx 5.0$ ev a value of $V_{i\ BaO} \approx$ ≈ 4.9 ev.

Assuming n = 1 also for the segment $T \gtrsim 400^\circ$ K, we have $Q_{10} \approx 3.5$ ev; hence, in accordance with the ionization potential, we obtain a lower value (~3.4 ev). Assuming n = 2, we have

$$Q_{10}^{+2} \approx 10\ ev, \quad V_{iBaO}^{+2} \approx 10\ ev\ (\text{for Ba } V_i^{+2} = 9.95\ ev).$$

These quantities appear more reasonable.

Thus, an application of the theory of ion vaporization to BaO on W suggests that BaO molecules should be desorbed by the field from tungsten in the form of singly charged ions at $T \gtrsim 400^\circ$ K and in the form of doubly charged ions at $T \approx$ $\approx 500 - 1100^\circ$ K.

On the basis of the $F_d(\Theta)$ function, described in Section 3, it is possible to roughly estimate the effective dipole moment μ per molecule, which is determined by the equation $\Delta\varphi = 4\pi n\mu$. According to Müller (Bibl.1, 6), we then have $F_{d\,|\Theta=1} - F_{d\,|\Theta=0} = F_{dip} \approx 9.05 \frac{\mu}{r^3}$, where $r = \sqrt{\frac{1}{n}}$. We assumed $n = 1.25 \times$ $\times 10^{14}$ cm^{-2} [$\varphi \sim 2.3$ ev (Bibl.5)] and obtained $\mu = 4.7$ D which, in view of the roughness of the estimate, is in excellent agreement with $\mu = 5.2$ D obtained elsewhere (Bibl.5, 13) from the function $\Delta\varphi(n)$.

It seems that a direct verification of these fairly unusual theoretical inferences would be of great interest.

5. Conclusions

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The results of this investigation reduce to the following:

1) No dissociation of BaO molecules was observed during their self-desorption from tungsten.

2) The temperature dependence of the desorbing field for BaO on W was

measured over the range of 80 - 1200° K.

3) A similar dependence was measured for the first time for Ba on W over the range of 80 - 300° K.

4) The findings were discussed on the basis of the Müller-Gomer theory of the vaporization of ions across the Schottky barrier.

5) It was established that, in the presence of low degrees of deposition, the components of mixed layers (Ba + BaO) on tungsten are individually stripped off.

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BIBLIOGRAPHY

1. Müller, E.W.: Advances in Electronics, Vol.13, p.83, 1960.
2. Gomer, R.: Field Emission and Field Ionization, Harvard Univ. Press, Cambridge, 1961.
3. Morgulis, N.D. and Gavrilyuk, V.M.: Zhurnal eksp. i teor. fiz., Vol.30, p.149, 1956.
4. Kirchner, F. and Ritter, H.: Zs. Naturforsch.,Vol.11a, p.35, 1956.
5. Vedula, Yu.S. and Gavrilyuk, V.M.: Ukr. fiz. zhurnal, Vol.3, p.632, 1958.
6. Müller, E.W.: Phys. Rev., Vol.102, p.618, 1956.
7. Cooper, E. and Müller, E.: Rev. Sci. Instr., Vol.29, p.309, 1958.
8. Drechsler, M. and Henkel, E.: Zs. angew. Phys., Vol.6, p.341, 1954.
9. Becker, J. and Brandes, R.: J. Chem. Phys., Vol.23, p.1323, 1955.

10. Ptushinskiy, Yu.G. and Chuykov, B.A.: Radiotekh. i elektronika, Vol.7, p.687, 1962; p.687, 1962.

11. Cape, J. and Coomes, E.: J. Chem. Phys., Vol.32, p.210, 1960.

12. Good, R.H. and Müller, E.W.: Handbuch d. Physik, Vol.21, p.176, 1956.

13. Morgulis, N.D.: Fiz. tverd. tela, Vol.1, p.1125, 1959.

14. Gomer, R.: J. Chem. Phys., Vol.31, p.341, 1959.

15. Vedula, Yu.S. and Gavrilyuk, V.M.: Ukr. fiz. zhurnal, Vol.5, p.816, 1960.

16. Glesston, S., Leydler, K., and Eyring, G.: Theory of Absolute Reaction Rates (Teoriya absolyutnykh skorostey reaktsiy). Moscow, IL Publ. House, 1948.

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